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SPECTRAL STUDY OF THERMOLUMINESCENCE EMISSION FROM KBr AND NaBr.

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ABSTRACT. The results obtained from the spectral study of thermoluminescence emission from KBr and NaBr coloured at 90°K by 10 KV electron bombardment are reported. An automatic rapid scanning quartz spectrophotometer capable of recording spectrum in one second is used to record the spectral distribution in the emission. The thermoluminescence of KBr consists of four strong glow peaks at approximately 163°K, 226°K, 330°K, and 498°K. Each of the first, second and the fourth glow peaks consists of a single band with maximum at 522mμ, 520mμ, 498mμ, respectively. There are two bands in the third glow peak with maxima at 443mμ and 516mμ. The thermoluminescence glow of NaBr is characterized by two strong glow peaks at about 145°K and 286°K and emission band maximum at 457mμ and 500mμ respectively.

INTRODUCTION

Colour centres are formed in alkali halides irradiated by ionizing radiations. There is bleaching and changes in some of these centres at specific temperatures, usually accompanied by thermoluminescence emission (Dutton *et al.*, 1953; Sharma, 1952, 1956, Halpern *et al* 1957). The results reported by different workers on luminescence emission at various temperatures together with the principal changes in colour centres, if there be any, are summarized in Tables I and II

It is to be seen from the tables that the findings of the different workers are not in accord with each other. This may in all probability be due to the differences in the nature and amount of irradiation, rate of heating, thermal history, physical nature and impurity contents of the phosphor

The present work deals with the behaviour and distribution of the spectral emission during thermoluminescence glow. The spectra recorded are shown in figures 1-4. The curve in each of the frame indicates the spectral and intensity distribution of the thermoluminescence glow with rise of temperature at an interval of one second. The area under each curve when plotted against its corresponding temperature gives the "glow curve"

EXPERIMENTAL TECHNIQUE

The spectral distribution of thermoluminescence is recorded by an automatic rapid scanning spectrophotometer, the construction of which was reported

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earlier (Dutta *et al* 1956). The finely ground phosphor (E. Merck, guaranteed reagent quality) is rubbed to the flat surface of the sample holder. A high rate of heating, 6°–7°C per second, is preferred so as to increase the intensity of emission. Care is taken to retain the purity of the sample

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

Potassium Bromide:

Potassium bromide fluoresces weakly on cathode ray bombardment at liquid oxygen temperature and the sample becomes blue on prolonged irradiation—

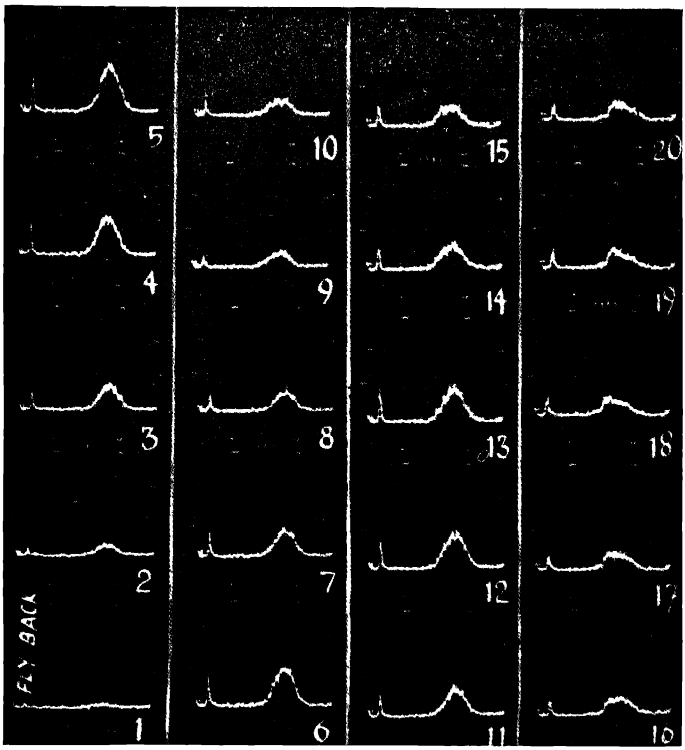

Fig. 1.—Thermoluminescence spectra of KBr irradiated by cathode rays at 90°K.

possibly due to *F* band (630 mμ). At low temperature the after-glow intensity is rather poor; but at high temperature it perceptibly increases. From the study of the shape and size of the glow curves (Sharma, 1956) and the corresponding spectra, it is found that the glow curves (except for the lowest temperature) are broad and extended, overlapping one another greatly; this means that the trap depths in this crystal are not as sharp as in the other crystals studied and lie distributed over wider limits.

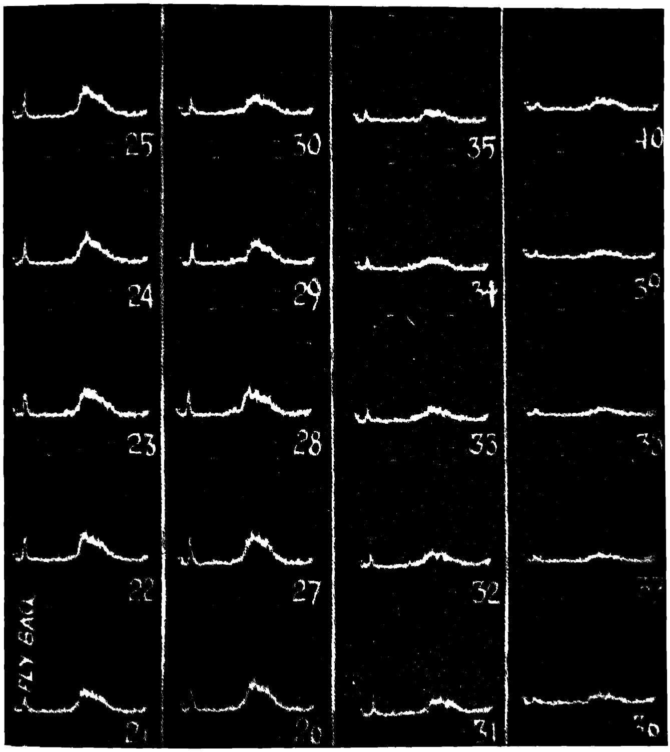

Fig. 2—Thermoluminescence spectra of KBr irradiated by cathode rays at 90°K. (*contd.*)

The thermoluminescence of KBr is characterised by four strong glow peaks at temperatures 163°K, 226°K, 330°K and 498°K. The spectra of the first two glow peaks seem to be identical. Immediately after the second glow peak, the effect of the third is reflected in the successive thermoluminescence spectra. The third glow peak is characterised by a strong short wave-length emission (443 mμ)

together with an indication of a long wave-length component (516 mμ) which persists over a wide temperature range. Either due to overlapping of the bands

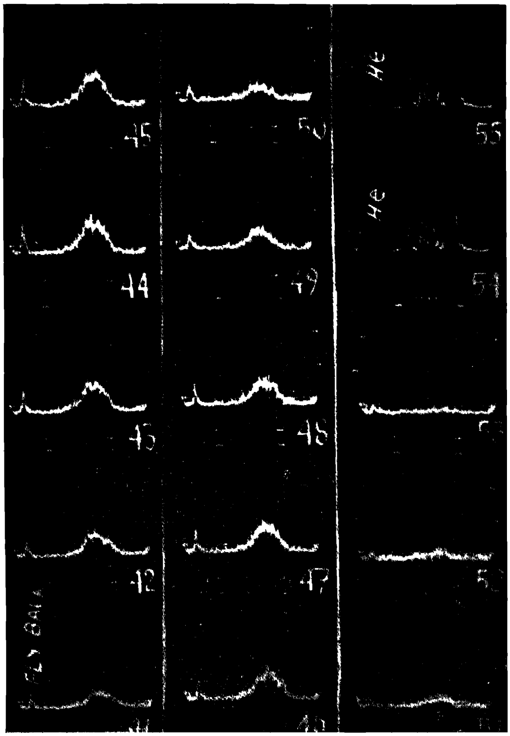

Fig. 3—Thermoluminescence spectra of KBr irradiated by cathode rays at 90°K. (*contd.*)

or due to temperature shift or due to both, the short wave-length band maximum of 443 mμ at 330°K appears to be shifted to 483 mμ at 402°K; the other band maximum ceases to be perceptible beyond ~370°K. The fourth glow spectrum is a single band. The position of the band maximum seems to remain completely unaffected by the temperature. The nature of the spectral emission of thermoluminescence of KBr will be evident from figures 1—4 and Table III.

It is observed that the blue colour of the sample disappears with the 163°K peak. Since thermal ionization of the *F* centre is improbable at this temperature, it may be that due to thermal ionization of V_1 centres holes are released and migrate to the *F* centres where recombination of the free holes and trapped electrons occur resulting in the destruction of the F centre, the cause of the blue colour of the sample. Dutton *et al.* (1953), reported such a phenomenon though at a somewhat lower temperature The spectrum of the second glow is a broad band and its emission occurs over a wide temperature range. The band maximum is compatible with that reported by Dutton *et al.* for the emission associated with the disappearance of the V_4-band. The process occurring during the third glow seems to be complex; the V_2 and V_3 bands are likely to be bleached in this temperature range. The thermoluminescence spectrum of the last glow is distinctly different from the others Possibly the thermal ionization of the F centre occurs at this temperature. By colouring the sample at room temperature the blue colour disappears in this temperature range.

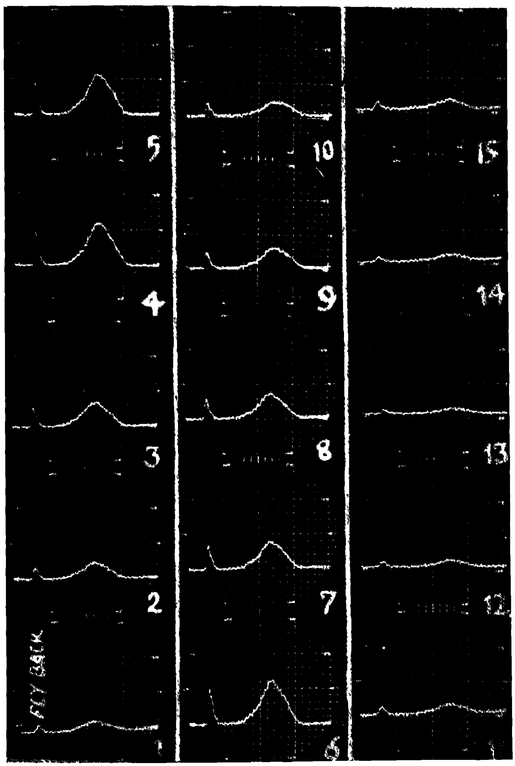

Fig. 4—Thermoluminescence spectra of NaBr irradiated by cathode rays at 90°K.

TABLE I

Luminescence peaks of KBr at various temperatures together with the principal changes in colour centres as reported by different workers.

Peak temperature in °K	Principal changes in absorption band	Luminescence peaks in $m\mu$	Method	Authors
115 143 185 225 246	V_1 F' [illegible] [illegible] V_4	$\lambda > 500$ $\lambda < 380$ $\lambda > 500$ — $\lambda > 500$	Luminescence glow and current peak measurement after X-ray irradiation at 90°K	Dutton and Maurer (1953)
123 203 263	– –	320 and 500 500 290 and 450	Phosphorescence glow measurement after γ-ray irradiation at nitrogen temp.	Ghormley and Levy (1952)
176 235 281 330 415 525	F – – – – –	– – – – –	Thermoluminescence and diffuse reflectance measurements after electron bombardment at 90°K.	Sharma (1956)
163 226 330 498	– – – –	522 520 433 and 516 498	Spectral study of Thermoluminescence by spectrophotometric method after electron bombardment at 90°K	Present authors.

TABLE II

Luminescence peaks of NaBr at various temperatures together with the principal changes in colour centres reported by different workers.

Peak temperature in °K	Principal change in absorption band	Luminescence peaks in $m\mu$	Method	Authors
133 194 225 300 480	– – – – F	– – – – –	Thermoluminescence and diffuse reflectance measurements after electron bombardment at 90°K.	Sharma (1956)
145 286	– –	457 500 and 570	Spectral study of thermoluminescence by spectrophotometric method after electron bombardment at 90°K.	Present authors

TABLE III

KBr

(Excited at liquid oxygen temperature)

Frame No.	Peaks $m\mu$	Half-width $m\mu$	Temperature °K
1	—	—	137
2	532	—	143
3	532	—	149
4	530	—	156
5 (Max)	522	476 — 589	163
6	527	—	170
7	527	—	178
8	527	—	186
9	535	—	194
10	535	—	202
11	535	—	210
12	525	—	218
13 (Max)	520	470 — 593	226
14	516	—	234
15	510	—	242
16	510	—	250
17	510	—	258
18	460	—	266
19	448 537	—	274
20	450 537	— —	282
21	450 526		290
22	443 526	—	298
23	443 516	—	306
24	443 516	—	314
25	443 516	—	322
26 (Max)	443 516	—	330
27	457		338
28	466	—	346
29	466 516	—	354
30	466 516	—	362
31	473		370
32	473		378
33	483	—	386
34	483	—	394
35	483	—	402
36 — 40	—	—	411 — 448
41	498	—	458
42	498	—	468
43	498		478
44	498	—	488
45 (Max)	498	448 — 582	498
46	498	—	508
47	498	—	518
48	498	—	528
49	498	—	538
50	498	—	548

TABLE IV

NaBr

(Excited at liquid oxygen temperature)

Frame No.	Peak $m\mu$	Half-width $m\mu$	Temperature °K
1	443	—	114
2	443	—	120
3	443	—	126
4	448	398 — 510	132
5	452	400 — 512	138
6 (Max)	457	418 525	145
7	461	418 525	152
8	461	418 525	159
9	463	426 — 530	166
10	465	426 — 530	174
11	476	445 — 546	182
12	482	449 — 558	190
13	482	—	198
14	—	—	206
15	498	—	230
16	507	460 — 580	238
17	507	460 — 580	246
18	507	460 — 583	254
19	510	460 — 583	262
20	498 551	450 590	270
21	500 551	445 — 600	278
22 (Max)	500 570	446 — 600	286
23	502 575	440 — 600	294
24	498	440 — 600	302
25	498	—	310
26	496	—	318
27	496	—	326
28	493	—	334
29	493	—	342

Sodium Bromide :

Sodium bromide has a bluish-green fluorescence–emission on cathode ray bombardment at liquid oxygen temperature NaBr even under prolonged irradiation cannot be visibly coloured It is to be noted that the phosphor is coloured yellow when heated to 250°K after irradiation at liquid oxygen temperature. This colour also appears on irradiating the sample at room temperature. Fluorescence emission of NaBr is characterised by an intense ultra-violet band extended from 350 $m\mu$ to 250mμ or beyond; other bands are also present in the visible region (Bose *et al.*, 1950).

The thermoluminescence of NaBr consists of two strong glow peaks at 145°K and 286°K. The spectral nature of the emission at different temperatures will be evident from figures 4 and 5 and Table IV. From a study of the nature of the emission, it is clear that the emission extends into the ultra-violet region; the ultra-violet part of the emission is missed because of the insensitivity of the phototube.

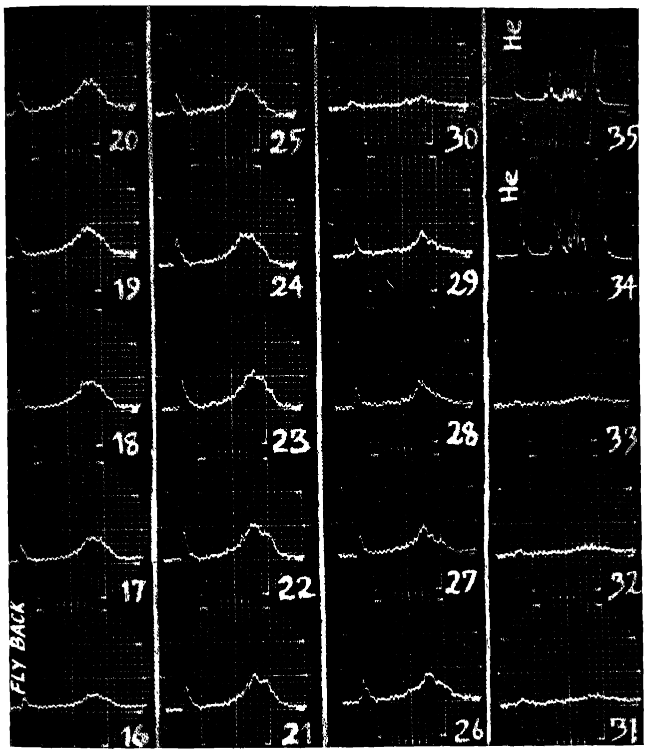

Fig. 5—Thermoluminescence of NaBr irradiated by cathode rays at 90°K. (*contd.*)

The lowest temperature glow peak occurs in the shorter wave-length region with band maximum at 457 mμ while the other one lies in the longer wave-length region with band maxima at 500 mμ and 570 mμ.

From the study of the emission it appears that there is a gradual change taking place throughout the process of thermoluminescence. Thus, for the first glow, emission at the initial and final stages has a band maximum at 443 mμ when the temperature is 114°K and at 482 mμ when the temperature is 198°K. During the second glow, initially, emission band maximum appears at 498 mμ corresponding temperature being 230°K; at about 270°K emissions show another long wave-length component with band maximum at 551 mμ. At the glow peak temperature 286°K there are two maxima in the emission band at 500 mμ and 570 mμ respectively.

If one takes into account the effect of mutual overlapping of two diffuse bands it can be easily seen that the development of a new diffuse band on the long wave-length side in the emission may cause the peak position of the original band to be shifted towards the longer wave-length. Thus it is reasonable to conclude that the emission band with maximum at 457 mμ(at 145°K), which is gradually shifted towards longer wave-length with increasing temperature, is present in all the glows observed.

Sodium bromide is a pronounced ultra-violet emitter; as such the measurements cannot be considered as complete for obvious reasons. From Table II we observe that Sharma associates the glow peak at 480°K, with the thermal bleaching of the F centre and it is assumed to be so. Due to its low intensity the spectrum of this glow could not be recorded. Comparing results with KBr and other phosphors it is guessed that the glow peaks at 145°K and 280°K are associated with the bleaching of the V_1 and V_4 centres. The additional long wave-length emission may be provided by the possible bleaching of the F' centres in the corresponding temperature range.

Additional work is needed before one tries to picture the kinetics of the emission process, and moreover the measurements, being confined to the visible region, are incomplete. Since absorption measurements have not been made, the identification of the glow peaks with thermal bleaching of the colour centres as reported are to be taken as suggestions rather than experimental findings.

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